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This grant was used to support research on (i) donor-induced interdiffusion in GaAs/AlAs superlattices, (ii) the structure and adatom diffusion on the stepped Si(100) surface, and (iii) the development a new, real-space multigrid method for electronic structure calculations. In GaAs, we used *ab initio* molecular dynamics to map out the diffusion process. Several competing pathways, involving either vacancies or interstitials, were considered. The results provide a microscopic picture of Si motion in both GaAs and AlAs and of the interdiffusion process. We have also developed a formalism that allows for calculations of free energy differences, and resolved an important controversy regarding the Ga vacancy in GaAs. On the Si(100) surface, we investigated the atomic and electronic structure of step edges by an *ab initio* method for the first time. Our simulated STM images are in very good agreement with experimental data, but change their interpretation. The diffusion paths and barried for adatoms across the buckled and stepped surface were determined. Finally, the real-space multigrid method is particularly suitable for very large scale calculations. The calculations use a grid as a basis and employ multigrid techniques, which results in preconditioning and convergence acceleration at all length scales.

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This grant was used to support research on (i) donor-induced interdiffusion in GaAs/AlAs superlattices, (ii) the structure and adatom diffusion on the stepped Si(100) surface, and (iii) the development a new, real-space multigrid method for electronic structure calculations. In GaAs, we used *ab initio* molecular dynamics to map out the diffusion process. Several competing pathways, involving either vacancies or interstitials, were considered. The results provide a microscopic picture of Si motion in both GaAs and AlAs and of the interdiffusion process. We have also developed a formalism that allows for calculations of free energy differences, and resolved an important controversy regarding the Ga vacancy in GaAs. On the Si(100) surface, we investigated the atomic and electronic structure of step edges by an *ab initio* method for the first time. Our simulated STM images are in very good agreement with experimental data, but change their interpretation. The diffusion paths and barried for adatoms across the buckled and stepped surface were determined. Finally, the real-space multigrid method is particularly suitable for very large scale calculations. The calculations use a grid as a basis and employ multigrid techniques, which results in preconditioning and convergence acceleration at all length scales.

During the grant period we worked on: (i) donor-induced interdiffusion in GaAs superlattices, (ii) entropic effects on diffusion in GaAs, (iii) the structure and electronic properties of single-height steps on Si(100), (iv) adatom diffusion on stepped Si(100) surface, and (v) development of a new, multigrid-based real space method for large scale electronic structure calculations. The results of these investigations are briefly summarized below, together with the list of papers, and invited and contributed talks supported by the grant.

Donor-induced interdiffusion in GaAs/AlAs superlattices

Ab initio molecular dynamic was used to study Si diffusion in GaAs and the Si-enhanced interdiffusion in GaAs/AlAs superlattices. Several competing diffusion pathways, involving either vacancies or interstitials, were considered. The results provide a microscopic picture of Si motion in both materials and of the interdiffusion process. The lowest energy diffusion path for Si on the Ga site involves second nearest neighbor jumps assisted by group III vacancies. Si-vacancy complexes are formed both when Si is introduced during growth and when it is in-diffused from the surface. This is due to the low formation energy of a negatively charged Ga vacancy in n-type material and to a Coulomb attraction between the vacancy and an ionized Si donor. The motion of the pair disorders the superlattice regardless whether Si was introduced during growth or in-diffused afterwards. This is in sharp contrast to acceptor-induced interdiffusion (e.g., by Zn), which requires in-diffusion after growth. The reasons for these differences are due to different diffusion mechanisms and are fully explained by the calculations.

Entropic effects can have a profound effect on defect concentrations and diffusion mechanisms in semiconductors. However, they are very difficult both to measure and to compute. We have recently developed a formalism to accurately compute finite temperature entropies completely from first-principles and applied it to the Ga vacancy in GaAs. The entropy of this vacancy has been recently extracted from Chemical Mapping experiments by Ourmazd and co-workers.[1] An unusually high value of 33 k_B was obtained. This created a substantial controversy, since such a large entropy, if correct, would imply that the current computed values of defect formation en-

1. J.-L. Rouviere, Y. Kim, J. Cunningham, J. A. Rentschler, A. Bourret, and A. Ourmazd, Phys. Rev. Lett. **68**, 2798 (1992).

ergies are wrong. (If they were combined with the entropy, the free energies of defects would be so small that the GaAs crystal would not be thermodynamically stable at room temperature.) Although Ourmazd's experiment involved atomic resolution microscopy, the entropy had to be extracted by fitting diffusion profiles and could thus be subject to errors.

We have developed a formalism that allows for accurate and efficient calculations of free energy differences. Briefly, it involves finite temperature simulations using quantum molecular dynamics at finite temperatures, in which the temperature is controlled very accurately using a chain of Nose-Hoover thermostats. Once this heat bath has been established, we carry out a "switching" transformation, due to Watanabe and Reinhardt, by adiabatically creating a vacancy in the system, or vice versa. The heat expended during this process provides an accurate, variationally bound measure of the free energy difference, and thus of the entropy. Our computed values bracket the entropy between 7 and 9 k_B, resolving the controversy. These results were discussed in an invited talk at the International Semiconductor conference in Vancouver. We still need to write a more complete description of the methodology and the results.

Papers

1. "Impurity-enhanced disordering in superlattices," J. Bernholc, B. Chen, Q. Zhang, C. Wang, and B. Yakobson, Mat. Sci. Forum 143-147, 593 (1994).
2. "Si diffusion in GaAs and Si-induced interdiffusion in GaAs/AlAs superlattices," B. Chen, Q.-M. Zhang, and J. Bernholc, Rapid Communications, Phys. Rev. B 49, 2985 (1994)
3. "Theory Of Diffusion In Gaas/Alas Superlattices," J. Bernholc, B. Chen, Q.-M. Zhang, C. Wang, S. K. Kajihara, and D. Sullivan, Proc. 22nd Conf. Phys. Semicond., edited by D. J. Lockwood, p. 2259 (World Scientific, 1995).

Theses

1. "Quantum Molecular Dynamics Simulations of Semiconductors," B. Chen, Ph. D. Thesis, August 1995.

Invited Presentations at Conferences

1. "Theory of Zn-Enhanced Disordering in GaAs/AlAs Superlattices," Q. Zhang, C. Wang, and J. Bernholc, ASM-TMS Symposium on Diffusion in Semiconductors, Denver, Colorado, February 1993.
2. "Theory of Diffusion in GaAs/AlAs Superlattices," J. Bernholc, B. Chen, C. Wang, and Q.-M. Zhang, APS March Meeting, Pittsburgh, Pennsylvania, 1994.
3. "Formation Entropies of Defects in Semiconductors," S. A. Kajihara, D. Sullivan, Q.-M. Zhang, and J. Bernholc, The Sixth Annual Workshop on Recent Developments in Electronic Structure Algorithms, Santa Barbara, California, June 1994.
4. "Theory of Diffusion in Gaas/AlAs Superlattices," J. Bernholc, B. Chen, Q.-M. Zhang, C. Wang, S. K. Kajihara, and D. Sullivan, 22nd Intern. Conf. on the Phys. of Semiconductors, Vancouver, Canada, August 1994.

Contributed Presentations at Conferences

1. "Theory of Zn-enhanced interdiffusion in GaAs/AlAs Superlattices," Q.-M. Zhang, C. Wang, and J. Bernholc, Bull. Am. Phys. Soc. 38, 338 (1993), APS March Meeting, Seattle, Washington.
2. "Theory of Si-enhanced Disordering in GaAs/AlAs Superlattices," B. Chen, Q.-M. Zhang, and J. Bernholc, Bull. Am. Phys. Soc. 38, 338 (1993), APS March Meeting, Seattle, Washington.
3. "Formation Entropies of Defects in Semiconductors," S. A. Kajihara, T. A. White, D. J. Sullivan, and J. Bernholc, Bull. Am. Phys. Soc. 38, 444 (1993), APS March Meeting, Seattle, Washington.
4. "Impurity-enhanced disordering in superlattices," J. Bernholc, B. Chen, Q. Zhang, C. Wang, and B. Yakobson, 17th Intern. Conf. on Defects in Semiconductors, Gmunden, Austria (1993).
5. "Formation entropies of defects in semiconductors," S. A. Kajihara, D. J. Sullivan, T. A. White, Q.-M. Zhang, and J. Bernholc, APS March Meeting, Pittsburgh, Pennsylvania, 1994.

Steps and growth on Si(100)

The Si (100) surface is usually preferred in MBE deposition and device growth. The structure, growth and energetics of this surface have been subject of many experimental and theoretical studies. Briefly, even the highest quality surfaces are known to contain steps (see Ref. [2] for an excellent review). These steps are one- or two-atomic layers high, depending on the miscut angle and temperature. For nominally flat surfaces (miscut angle smaller than 1.5 degrees), monolayer high steps dominate. In recent years, it has become apparent that steps play a crucial role in controlling the growth processes on the (100) surface: at standard temperatures, adatoms that have condensed on the flat regions of the surface (terraces) diffuse to the step edges, where they are more readily incorporated into the crystal. This step-flow mechanism results in the desired layer-by-layer epitaxial growth. The step-flow mechanism operates not only for homoepitaxy, but also for heteroepitaxy of III-V systems.[3] To understand the step-flow mechanism, one needs to know the surface diffusion of adatoms, and their binding energies at the step edges.

We investigated the atomic and electronic structure of step edges by quantum molecular dynamics. Our results showed that the ground state step configurations are insulating, and that buckling at step edges considerably alters their geometry.[4] Our simulated STM images were in very good agreement with experimental data. In particular, they explained the differences between the filled- and empty-state images as being due to differences in the shape of valence and conduction bands wavefunctions. (These differences were previously attributed to tip-induced reconstructions.[2]) We have also carried out adiabatic trajectory simulations of the preferred low temperature diffusion pathways. Surprisingly, the diffusion barriers are also sensitive to the local buckling of the dimers. This is because the tilt of the dimer can follow the diffusing adatom. The adatom binding energies and escape barriers at step edges depend strongly on the type of the step. The so-called S_A step edge,[5] where the dimers on the upper terrace are oriented perpendicular to the step edge, is a relatively poor sink for adatoms, while adatoms can be easily trapped at the S_B edge, where the

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2. J. E. Griffith and G. P. Kochanski, CRC Crit. Rev. Solid State Mat. Sci. **16**, 255 (1990).
3. M. T. Suchiya et al, Phys. Rev. Lett. **62**, 466 (1989).
4. P. Boguslawski, Z. Zhang, Q. Zhang, and J. Bernholc, Phys. Rev. Lett. **72**, 3694 (1994).
5. D. J. Chadi, Phys. Rev. Lett. **59**, 1691 (1987).

dimers on the upper terrace are oriented parallel to the step edge. These results explain the fast growth observed at the ends of the dimer rows, and thus the dominance of S_B motion in step-flow growth of Si, as well as shape evolution of islands during deposition.[6] Our results differ significantly from those obtained for the flat unbuckled surface[7] by the Car-Parrinello method, and from predictions based on classical potentials for the step edges.[8]

Papers

4. "Structure of monoatomic steps on Si(100) surface", P. Boguslawski, Z. Zhang, Q. Zhang, and J. Bernholc, Phys. Rev. Lett. 72, 3694 (1994).
5. "Structure of Si(001) surface with monoatomic steps", P. Boguslawski, Z. Zhang, Q. Zhang, and J. Bernholc, MRS Symp. Proc. in press.
6. "Ab initio studies of single-height Si(001) steps," P. Boguslawski, Q.-M. Zhang, Z. Zhang, C. Roland, and J. Bernholc, Mat. Sci. and Eng. (B): Solid State Materials for Adv. Techn. 30, 167(1995).
7. "Ab Initio Studies of Si (100) Steps of Monoatomic Height: Structure and Diffusion Barriers," C. Roland, P. Boguslawski, Q.M. Zhang, Z. Zhang and J. Bernholc, Proc. 22nd Conf. Phys. Semicond., edited by D. J. Lockwood, p. 493 (World Scientific, 1995).
8. "Ab Initio Studies of the Diffusion Barriers of Single-Height Si (100) Steps," Q.-M. Zhang, C. Roland, P. Boguslawski, and J. Bernholc, Phys. Rev. Lett. 75, 101 (1995).

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5. "Structure of Si(001) surface with monoatomic steps," P. Boguslawski, Z. Zhang, Q. Zhang, and J. Bernholc, European Research Conference on Electronic Structure of Solids: Surfaces, Interfaces, and Localized Defects, Thessaloniki, Greece, September 1993.
6. "Quantum Molecular Dynamics Simulations of Materials Properties," J. Bernholc, Third Conference on Computational Research on Materials, Morgantown, West Virginia, May 1993.

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6. For an excellent overview, see M. G. Lagally, Physics Today, November 1993.
7. G. Brocks, P. J. Kelly and R. Car, Phys. Rev. Lett. **66**, 1727(1991).

7. "Quantum Molecular Dynamics Simulations of Materials," J. Bernholc, in Tutorial NSF Supercomputer Centers: What do they offer, APS March Meeting, Pittsburgh, PA, March 1994.
8. "Ab Initio Molecular Dynamics on the Cray T3D," Q.M. Zhang, V. Shaffer, P. Boguslawski, C.M. Roland, and J. Bernholc, The Sixth Annual Workshop on Recent Developments in Electronic Structure Algorithms, Santa Barbara, California, June 1994.
9. "Structure of steps on Si(100) surface and ad-atom diffusion," J. Bernholc, P. Boguslawski, C. Roland, Q. Zhang, and Z. Zhang, Electronic Materials Conference, Boulder, Colorado, June 1994.
10. "Ab initio studies of the diffusion of Si ad-atoms over flat and stepped Si(100) surfaces," C. Roland, Q.-M. Zhang, M. G. Wensell, P. Boguslawski, and J. Bernholc, Fourth International Conference on Advanced Materials, Cancun, Mexico, August 1995.
11. "Ab Initio Simulations of Materials," PATP Scientific Conference, Pasadena, California, August 1995.
12. (Plenary) "Supercomputer simulations of advanced materials," J. Bernholc, High Performance Computing - Asia 95, Taipei, Taiwan, September 1995.
13. "*Ab Initio* Simulations of Materials," J. Bernholc, P. Boguslawski, C. Brabec, E. L. Briggs, A. Maiti, C. Roland, D. J. Sullivan, M. Wensell, Q.-M. Zhang and Z. Zhang, International Symposium on the Science and Technology of Atomically Engineered Materials, Richmond, Virginia, November 1995.
14. "Simulations of crystal growth: Step flow and low-temperature growth," C. Roland, G. H. Gilmer, Q.-M. Zhang, P. Boguslawski, and J. Bernholc, MRS Fall Meeting, Boston, Massachusetts, December 1995.

Contributed Presentations at Conferences

6. "Structure of monolayer steps on Si(001) surface by *ab initio* molecular dynamics," P. Boguslawski, Z. Zhang, Q. Zhang, and J. Bernholc, APS March Meeting, Seattle, Washington (1993).

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8. a) J. Wang and A. Rockett, Phys. Rev. B **43**, 12571 (1991); b) Z. Zhang, Y. Lu and H. Metiu, Surf. Sci. **80**, 1248 (1991); c) C. Roland and G. H. Gilmer, Phys. Rev. B **46**, 13 428 (1992).

7. "Structure of Si(001) surface with monoatomic steps," P. Boguslawski, Z. Zhang, Q. Zhang, and J. Bernholc, MRS Fall Meeting, Boston, Massachusetts (1993).
8. "Si(001) surface with monoatomic steps and ad-atom diffusion," Q.-M. Zhang, P. Boguslawski, Z. Zhang, C. Roland, and J. Bernholc, APS March Meeting, Pittsburgh, Pennsylvania, 1994.
9. "Ab Initio Studies of Si (100) Steps of Monoatomic Height: Structure and Diffusion Barriers," C. Roland, P. Boguslawski, Q.M. Zhang, Z. Zhang and J. Bernholc, 22nd Intern. Conf. on the Phys. of Semiconductors, Vancouver, Canada, August 1994.
10. "Ab initio study of the diffusion barriers of single-height Si (100) steps," Q.-M. Zhang, C. Roland, P. Boguslawski, and J. Bernholc, APS March Meeting, San Jose, California, 1995.
11. "Finite Temperature Simulations of Si Adatom Diffusion on Flat and Stepped Si(100) Surfaces," M. G. Wensell, C. Roland, J. Bernholc, and Q.-M. Zhang, APS March Meeting, San Jose, California, 1995.

A new real-space multigrid method for large scale calculations

We have developed a new method for electronic structure calculations that is particularly suitable for very large scale calculations. The calculations occur entirely in real space and use a grid as a basis. This allows us to employ multigrid techniques, that result in preconditioning and convergence acceleration at all length scales. We have carried out tests on a variety of systems. Whenever a direct comparison was possible, the multigrid results agreed very well with those obtained by plane wave Car-Parrinello methods. However, the multigrid techniques allow for studies of much more difficult systems, such as transition metal interfaces, first-row adsorbates, and systems that exhibit convergence instabilities, e.g., due to charge sloshing. The real space nature of the method, together with the convergence acceleration features of multigrid, makes it an excellent candidate for the so-called O(N) methods, that would allow calculations for much larger systems. Very recently, we have ported this code to the massively parallel Cray T3D system. This was a significant effort, and much of the code needed to be re-written in order to execute effectively across many processors. However, the real space aspects of the method allowed for a very efficient parallelization, using the so-called data decomposition techniques, in which each processor is

assigned a fixed fraction of the volume and all communication remains local. The resulting code scales completely linearly with the number of processors, in all the cases we tried (up to 128). We have already carried out calculations with more than 400 atoms on the T3D, and further applications are in progress. I believe that these are by far the largest calculations to date that used real-space methodology.

This work has been very well received by the scientific community. Although we have only written one paper on this topic, which has appeared only very recently, we have already been asked to deliver three invited talks, including the opening talk at the Electronic Structure 95 Workshop. The PI has also been asked to be the US co-organizer of the workshop on Grids, Splines, and Wavelets in Electronic Structure Methods, to be hosted by CECAM (Lyon) in 1996.

Papers

9. "Large Scale Electronic Structure Calculations Using Multigrid Methods, E. L. Briggs, D. J. Sullivan and J. Bernholc, in High Performance Computing 1995, edited by A. Tentner, p. 153 (The Society for Computer Simulation, 1995).
10. "Large Scale Electronic Structure Calculations with Multigrid Acceleration," , E. L. Briggs, D. J. Sullivan and J. Bernholc, Rapid Communications, Phys. Rev. B 52, R5471 (1995).

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15. "Large scale electronic structure calculations using multigrid methods." E. L. Briggs, D. J. Sullivan, and J. Bernholc, High Performance Computing Symposium 95 at the Simulation Multi-Conference, Phoenix, Arizona, April 1995.
16. "Electronic Structure Calculations on a Real Space Mesh with Multigrid Acceleration," E. L. Briggs, D. J. Sullivan, C. J. Brabec, and J. Bernholc, Seventh Annual Workshop on Recent Developments in Electronic Structure Algorithms, St. Mary's City, Maryland, May 1995.
17. "Electronic Structure Calculations on a Real Space Mesh with Multigrid Acceleration," D. J. Sullivan, E. L. Briggs, C. J. Brabec, and J. Bernholc, MRS Fall Meeting, Boston, Massachusetts, December 1995.

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12. "Electronic Structure Calculations using an Adaptive Real-Space Basis with Multilevel Convergence Acceleration," D. J. Sullivan, E. L. Briggs, and J. Bernholc, Bull. Am. Phys. Soc. 38, 89 (1993), APS March Meeting, Seattle, Washington.
13. "Real space basis with multilevel convergence acceleration," D. J. Sullivan, E. L. Briggs, and J. Bernholc, APS March Meeting, Pittsburgh, Pennsylvania, 1994.
14. "Large Scale Electronic-Structure Calculations with Multigrid Acceleration," E. L. Briggs, D. J. Sullivan, and J. Bernholc, APS March Meeting, San Jose, California, 1995.
15. "Molecular Dynamics with Multigrid Acceleration Using a Real-Space Basis," D. J. Sullivan, E. L. Briggs, and J. Bernholc, APS March Meeting, San Jose, California, 1995.
16. "Electronic Structure Calculations on a Real Space Mesh With Multigrid Acceleration," J. Bernholc, E. L. Briggs, D. J. Sullivan and C. J. Brabec, Fourth International Conference on Advanced Materials, Cancun, Mexico, August 1995.